PATENT ABSTRACTS OF JAPAN

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(54) CERAMIC FILTER AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To improve thermal shock resistance by compacting and sintering a mixture of amorphous glass power consisting of specified amts. of silica, alumina and magnesia components with a spherical pore imparting material and using the resultant porous body having a signal phase of cordierite and mainly contg. spherical pores.

SOLUTION: Amorphous glass powder consisting of 40-65 wt.% silica component, 25-45 wt.% alumina component and 10-16 wt.% magnesia component is adjusted to ≤20 μm particle diameter, mixed with a spherical pore imparting material, compacted and sintered and the resultant porous body having a single phase of cordierite and mainly contg. spherical pores is used to produce the objective ceramic filter used as a catalyst carrier for exhaust gas from an automobile and as a filter for removing ash contained in waste combustion gas, etc. The apparent porosity and average pore diameter of the porous body are regulated to 25-50% and 10-100 μm, respectively. The amorphous glass powder adjusted to ≤20 μm diameter is preferably granulated before the mixing.

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CLAIMS

[Claim(s)]
[Claim 1] The ceramic filter characterized by a silica component consisting of a porous body which makes a subject the cordierite single phase and spherical pore which an alumina component fabricates only the amorphous glass powder 25 - 45 % of the weight and whose magnesia component are 10 - 16 % of the weight, and it comes to sinter 40 to 65% of the weight as a porous body formation ingredient.
[Claim 2] The ceramic filter according to claim 1 whose apparent porosity of a porous body is 25 - 50%.
[Claim 3] The ceramic filter according to claim 2 whose average pore diameter of a porous body is 10-100 micrometers.
[Claim 4] The manufacture approach of the ceramic filter which an alumina component uses only the amorphous glass powder 25 - 45 % of the weight and whose magnesia component are 10 - 16 % of the weight, and adjusts this powder to the particle size of 20 micrometers or less, and a silica component adds spherical pore grant material to this 40 to 65% of the weight, and consists of a cordierite single phase characterized by mixing, fabricating and sintering as a porous body formation ingredient.
[Claim 5] The manufacture approach of the ceramic filter according to claim 4 which corns the amorphous glass powder adjusted to the particle size of 20 micrometers or less, and adds spherical pore grant material to this.
[Claim 6] The manufacture approach of the ceramic filter according to claim 4 or 5 which consists of a porous body which uses an organic substance spherule as spherical pore grant material, and makes spherical pore a subject.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the ceramic filter which consists of a cordierite single phase which is excellent in thermal resistance and thermal shock resistance, and has uniform predetermined pore diameter distribution, and its manufacture approach. Since 1 - 2x10-6/degree C, a small thing, and Young's modulus are below one half of 150 or less GPas and an alumina, thermal shock resistance and heat-resistant stress nature are high, and as for cordierite ceramics, the coefficient of thermal expansion is broadly used as a filter for combustion ashes clearance contained in the catalyst support for automobile exhaust, combustion gas, etc. with the ingredient which gave porosity taking advantage of the advantage which is excellent also in the chemical stability at the time of an elevated temperature.
[0002]
[Description of the Prior Art] Heating to a 1300-1400-degree C elevated temperature, using the powder or these chlorides of a silica, an alumina, and a magnesia as an example of the manufacture approach of the conventional cordierite sintered compact, and considering as a cordierite sintered compact from the solid phase reaction is known.
[0003] And the manufacture approach which produces the porous body to which the melting point is low, or it mixes, fabricates, and sinters [the ingredient which generates the liquid phase is used as binding material, and] below with the melting point, and pore exists between particles from cordierites, such as a feldspar which grinds this sintered compact and contains a sieve part opium poppy, Na, calcium, K, etc. in a fixed particle size in order to consider as the target pore diameter in the case of a porous body, beta-spodumene which is lithium aluminium silicate, and eucryptite, is common.
[0004] However, by this conventional manufacture approach, since cordierite was a difficulty degree of sintering, the melting point was lower than cordierites, such as beta-spodumene which is lithium aluminium silicate as a binding material, eucryptite, or a feldspar (aluminosilicate) containing Na, calcium, and K, or in order to use the ingredient which generates the liquid phase below with the melting point, there was a fault to which thermal resistance falls.
[0005] For example, in JP,1-297131,A, the manufacture approach of the cordierite porous body which adds to cordierite the beta-spodumene and eucryptite which are lithium aluminium silicate, and has the target pore diameter at it is indicated. The melting point of this eucryptite is about 1400 degrees C. Therefore, since it is lower than the melting point (1470 degrees C) of cordierite used as a principal component, thermal resistance falls. If it sinters by furthermore mixing with cordierite, in order to generate and sinter the liquid phase from near 1100 degree C, there is a fault which cannot be used at the temperature beyond it.
[0006] Moreover, when the feldspar (aluminosilicate) containing Na, calcium, and K is used as binding material, since it is high as compared with 4 - 6x10-6/degree C and cordierite, the coefficient of thermal expansion of binding material raises the coefficient of thermal expansion as a sintered compact, and may reduce thermal shock resistance.
[0007] In JP,3-10365,A, talc, a magnesite, a magnesium carbonate, Although the manufacture approach of the cordierite porous body which mixed the quartz, the calcite, the aluminum hydroxide, etc. and was porosity-ized from chemical reactions, such as decomposition of magnesium salt, such as a magnesium hydroxide and a magnesium carbonate, and sublimation, is indicated Since pore is produced at the pyrolysis reaction etc., the porous body manufactured by this approach turns into a porous body which takes large pore diameter distribution, and has the fault which cannot obtain a uniform porous body with pore diameter distribution of a desired pore diameter easily.
[0008] In JP,60-226416,A, an aluminum metal salt and a magnesium metal salt are melted into the alcoholic solution of alkyl silicate, in a heating zone, it fuses and the manufacture approach of a cordierite porous body by the fuel spray and producing and sintering [fabricate and] the glass hollow ball of fines of having the detailed pore whose average pore diameter is less than 1 micrometer - several micrometers is indicated. Although this approach is suitable for a pore diameter producing the porous body which has several micrometers or less, high porosity, and detailed pore at 48% or more of porosity, it has a fault with production of the porous body of less than 48% of porosity and an average pore diameter difficult for production of 10 micrometers or more and a cordierite porous body especially with the big pore diameter of 50 micrometers or more.
[0009] In JP,57-92574,A, it is indicating using the raw material which consists of the glass powder of a cordierite presentation, the kaolin and talc which deposit cordierite by baking, and an aluminum oxide. This approach is not enough in that mixing of an impurity is not avoided since a raw material is a natural mineral, but the lowering on the strength in that result elevated temperature takes place, although a raw material is comparatively cheap and fits a certain kind of the manufacture approaches, such as extrusion molding.
[0010] Thus, the essential problem of the above existing technique While using the cordierite excellent in the coefficient of thermal expansion, since other components were added in order to improve the degree of sintering, and the porous body has been obtained, the property of construction material is not utilizable enough, In JP,60-226416,A, the porosity range is not suitable for that configuration control of the pore which forms a porous body cannot carry out to arbitration, and a pan. Moreover, when there was a problem that the mechanical strength for functioning as an elevated-temperature gas filter is not enough etc. and each was used as an elevated-temperature gas filter, the problem was in durable dependability over a long period of time.
[0011]
[Problem(s) to be Solved by the Invention] This invention makes these conventional technique a background, thermal resistance is high and it excels in thermal shock resistance, and it is chemically stable, and it is a spherule mostly and a pore configuration aims to let the pore diameter distribution offer the ceramic filter using a uniform cordierite porous body.
[0012]
[Means for Solving the Problem] As for this invention, a silica component offers the ceramic filter characterized by consisting of a porous body which makes a subject the cordierite single phase and spherical pore which fabricate and come to sinter only the

amorphous glass powder with which 25 - 45 % of the weight and a magnesia component consist [40 - 65 % of the weight, and an alumina component] of 10 - 16 % of the weight as a porous body formation ingredient.
[0013] Moreover, the manufacture approach of the ceramic filter which consists of a cordierite single phase to which a silica component is characterized by adding [40 - 65 % of the weight and an alumina component use only the amorphous glass powder with which 25 - 45 % of the weight and a magnesia component consist of 10 - 16 % of the weight, and adjust this powder to the particle size of 20 micrometers or less, and] spherical pore grant material to this and sintering [mix, fabricate and] as a porous body formation ingredient is offered.
[0014] In the desirable mode of the ceramic filter of this invention, the apparent porosity of a porous body is 25 - 50%. In the still more desirable mode of the ceramic filter of this invention, the average pore diameter of a porous body is 10-100 micrometers.
[0015] In the desirable mode of the manufacture approach of this invention, the amorphous glass powder adjusted to the particle size of 20 micrometers or less is corned, and spherical pore grant material is added to this. In another desirable mode of the manufacture approach of this invention, an organic substance spherule is used as spherical pore grant material, and it consists of a porous body which makes spherical pore a subject.
[0016] Since cordierite is a difficulty degree of sintering as above-mentioned, in a crystallization object simple substance, it is hardly sintered and cannot obtain the porous body with which between particles was combined firmly. When the powder used as a drive unit ingredient which forms a porous body considers only as amorphous glass and pulverizes and sinters this, this invention persons An average pore diameter by using the spherical pore formed after the organic substance sphere which was made to discover firm association and was added as a desirable approach is burned down at the time of baking, without adding binding material 10-100 micrometers, It found out that the ceramic filter with which 40-60-micrometer spherical pore consists of a porous body of the cordierite single phase distributed to homogeneity especially could be manufactured.
[0017]
[Embodiment of the Invention] The start raw material of the amorphous glass used for this invention is good as corundum and a source of a magnesia (MgO) as a source of a silica (SiO2) at magnesium salt or magnesium hydroxides, such as a magnesium carbonate and a magnesium nitrate, etc. as the silica sand produced naturally and a source of an alumina (aluminum 2O3). raw material purity has [every raw material] especially desirable ** 98% or more 95% or more. The presentation of the porous body which consists of a cordierite single phase from which purity is obtained after crystallization at less than 95% with the impurity contained in a raw material shifts, and there is a possibility that heat-resistant lowering and buildup of a coefficient of thermal expansion may take place.
[0018] The reason to which the magnesia component limited [the silica component / the alumina component] the presentation of a glass marble with 10 - 16 % of the weight 25 to 45% of the weight 40 to 65% of the weight is because the porous body of a cordierite single phase is not obtained after heating (sintering) processing but the alumina which is a mullite, forsterite, a spinel, or a start raw material, a silica, and a magnesia deposit as a mixed phase in this presentation out of range.
[0019] In addition, it is convenient even if the component and impurity of little others are contained as a presentation of glass in extent which does not spoil these objects. Moreover, when using alumina balls in wet grinding performed for pulverizing, about the amount of aluminas mixed from the ball wear at the time of the grinding, it is desirable by reducing the amount of aluminas of initial addition a little to make it a gap of a presentation not take place.
[0020] In addition, it sets to this invention and a cordierite single phase is xMgO-yAl2 O3 and zSiO2 as a cordierite crystal. The crystal phase contained in the range which sets and is shown by x:1.5-2.6, y:1.5-2.4, and z:4.1-6.4 is said.
[0021] The manufacture approach of the amorphous glass used for this invention and its powder is as follows. The raw material to be used is fully fused above 1500 degrees C with a commercial electric furnace after desiccation. In order to obtain a thing precise as a vitreous humour, fusing above 1600 degrees C is desirable. Especially an electric furnace is not limited but should just become 1500 degrees C or more. In order to obtain ejection and amorphous glass from an electric furnace, as for the melt obtained with the electric furnace, it is desirable to supply underwater and to quench. on a griddle, a copper plate, etc., sink appearance may be carried out and you may quench.
[0022] In this way, the obtained amorphous glass is ground in magnitude with a particle size of about 1-3mm. It grinds to the particle size of 150 micrometers or less using equipments, such as a vibration mill, after that. Wet grinding of the obtained powder is further carried out by the mono-chestnut pot. The quality of a dispersion medium at the time of grinding has water or desirable alcohol. When using water, the high concentration slurry of 30 - 40 volume % is obtained by carrying out proper amount addition of the suitable dispersant.
[0023] As for slurry concentration, grinding time amount, etc., it is desirable to set up so that the particle size of the powder obtained after grinding may be set to 20 micrometers or less. In 20-micrometer **, particle size can serve as a source of stress concentration in which the reinforcement of a porous body is reduced, when near and uniform spherule pore cannot be formed in the magnitude of the organic substance spherule of a pore grant agent which more than one half of raw materials for glass mentions later and those big particles condense.
[0024] The above grinding slurry is dried. When alcoholic grinding is carried out, the vacuum drying by the evaporator is performed. Moreover, granulation desiccation according to spray dry in the case of water grinding is sufficient.
[0025] In this way, in order to make spherical pore give the amorphous glass powder which brings about the prepared cordierite presentation, an organic substance spherule is added preferably. Although the organic substance spherule to add can use various things, an acrylic, polystyrene, PMMA (polymethyl methacrylate) of the thing of the resinic body comparatively burned and decomposed at low temperature, etc. are desirable.
[0026] It considered as the spherule by making spherical the configuration of the pore obtained after combustion for raising the reinforcement of the sintered compact which is made to reduce the stress concentration at the head of a crack at the time of destruction of a porous body, and consists only of amorphous glass powder. Many of grant material other than the organic substance, such as graphite powder usually used as pore grant material, has the comparatively high temperature understood a burned part at the time of sintering, and since fluctuation of the oxygen tension in a firing furnace is very hard to decompose, generally it is not desirable.
[0027] Moreover, although it can be chosen in consideration of the pore diameter of the ceramic filter made into the object, if it carries out from it being suitable for clearance of the particle in the dusty gas which the ceramic filter of this invention generates from coal combustion, the about 20-100-micrometer thing which was suitable for forming about 10-100-micrometer pore as an average pore diameter in consideration of the magnitude of the particle, the pressure-loss property at the time of a filter activity, etc. is suitable for the magnitude of a spherule.
[0028] moreover -- although it is related to the porosity of the porous body obtained as a mixed rate to amorphous glass powder -- 50 - 80 % of the weight of glass powder -- receiving -- pore grant material -- about 20 - 50 % of the weight is desirable.
[0029] The granulation powder which is also effective as for using as granulation which corned beforehand in the condition that it may collapse [in / on the occasion of shaping / although a thing 20 micrometers or less is used as amorphous glass powder in this way by

the manufacture approach of this invention / application of pressure] easily for the original particle, and was used as about 40-100-micrometer granulation using impalpable powder 20 micrometers [such] or less is also contained in the powder 20 micrometers or less of this invention.
[0030] That is, if the configuration can be held also at the time of sintering, a granulation object has the advantage which can reduce the addition of pore grant material, and also has the advantage which is easy to mix the granulation, then both of magnitude comparable as the spherical pore grant material to add. Moreover, in this invention, it is also mixable with other glass powder in the condition of having made the amorphous glass powder of a particle adhering to the perimeter of pore grant material beforehand.
[0031] Shaping in this invention and especially the sintering approach are not limited, but should just fabricate the mixed powder obtained by the above-mentioned approach by approaches, such as metal mold shaping and extrusion molding. The acquired Plastic solid should just sinter in 1000-1450 degrees C using electric furnaces, such as resistance heating. In addition, it is more desirable to establish the holding time in a maximum temperature, in order to promote crystallization of glass.
[0032] By the above approach, the same [as that of the added organic substance spherule / almost] or the sintered compact with which the hole which made the subject the shape of a ball of a little small average pore diameter consists of a cordierite single phase distributed to homogeneity can be manufactured. Thus, according to this invention, the cordierite porous body of the pore diameter of the object from which the pore diameter was distributed over homogeneity can be manufactured, without spoiling thermal resistance and thermal shock resistance. That the hole in a sintered compact is a spherule has little stress concentration as a defect, when the load of the stress is carried out as the structure, and reinforcement high as a result is given.
[0033] In addition, in this invention, the porous body which makes spherical pore a subject means a porous body which forms the pore in the condition with which spherical pores connected the part mutually that the pore in which many configurations of each pore have a sharp angle hardly exists while having connected by pore so that it may be spherical and such pores may turn into puncturing pore mutually.
[0034] The apparent porosity in which the porous body of such this invention is suitably used as a target ceramic filter mentioned above, and it deals is as large as 25 - 50%, and an average pore diameter is also obtained as what was easily controlled in the thing of 10-100 micrometers and the big aperture especially as a pore diameter of 40 micrometers or more. Moreover, the range of the above-mentioned average pore diameter also has pore diameter distribution, and that by which 80% or more of the total pore volume goes into **20% of within the limits from an average pore diameter desirably is obtained easily.
[0035] Thus, since it consists of a cordierite single phase, the filter manufactured by the manufacture approach of this invention has a very low coefficient of thermal expansion, it is chemically stable, and it is the optimal as an ingredient of the filter which performs the dust removal in elevated-temperature gas. Moreover, since pore is spherical, reinforcement is also high, and it excels also in durable dependability over a long period of time.
[0036]
[Example] Although an example and the example of a comparison are given to below and explained to it in more detail, this invention is not limited to these.
[0037] (Example 1) It ****(ed) so that it might become 49.5 % of the weight of silicas, 37.2 % of the weight of alpha-aluminas, and 13.3 % of the weight of magnesias, and after mixing, using the resistance heating-type electric furnace, it held at 1600 degrees C for 5 hours, and it dropped underwater and the amorphous vitreous humour was obtained after melting. Coarse grinding of the obtained glass was carried out to the particle with a particle size of 150 micrometers or less by the dry type planetary mill. Wet grinding of the end of coarse powder it was obtained was further carried out by the mono-chestnut pot. Water was used as an alumina and quality of a dispersion medium as a ball. Raw material concentration is 35 volume %, and grinding time amount is 24 hours.
[0038] The particle diameter after grinding was 20 micrometers or less, and mean particle diameter was 4.8 micrometers. The slurry after grinding carried out desiccation granulation with the spray dryer as it was after ejection from the pot. The rotational frequency of an atomizer is [140 degrees C and the outlet air temperature of 8000rpm and inlet-port air temperature] 80 degrees C. The mean particle diameter of dry granulation was 47 micrometers.
[0039] The obtained granulation was blended dryly by the sphere made from an acrylic (mean particle diameter of 60 micrometers), and V mixer. The mixing ratio of an acrylic sphere is 30 % of the weight, and mixing time could be 30 minutes. 60mmx120mm metal mold is filled up with the obtained powder, and they are 200 kgf/cm2 with a press-forming machine. It fabricated by the pressure. The acquired Plastic solid was calcinated in the resistance heating furnace in 1350-degree-C 2 hours. The obtained sintered compact was a cordierite single phase, and the apparent porosity was 32%.
[0040] Distribution of the pore in a sintered compact was almost uniform, and the average pore diameter was 43 micrometers. 83% of the total pore volume existed in **10% of within the limits from the average pore diameter, and pore diameter distribution showed the high pore diameter controllability. Moreover, the hole with which some spherical pores connected the configuration of the obtained pore on the basis of the shape of a ball was formed selectively, and there is almost no sharp pore used as the source of stress concentration, and the desirable organization was obtained also from the point of the reinforcement of a porous body.
[0041] In order to evaluate the high temperature strength and chemical stability of a porous body which were obtained, the flexural strength between heat (1000 degrees C) was measured. Moreover, the reinforcement was measured after being exposed to 900-degree-C elevated-temperature gas containing the sulfide of the same presentation as the exhaust gas of a coal combustion plant. The above result is shown in a table 1.
[0042] Moreover, to a table 1, the test result of the ingredient (example 1 of a comparison) of the same porosity which used lithium aluminosilicate for the binding material used from the former was also written together. this invention porous body which consists of a cordierite single phase does not almost have lowering on the strength between heat, and did not cause lowering on the strength at all under corrosive gas. Therefore, if it uses as a filter used for the heat indirect desulfurization dust of a coal power generating plant, it can be used, without spoiling dependability for a long period of time. Furthermore, the Weibull modulus (measurement with the flexural strength between heat) which shows dispersion in the reinforcement of the ceramics had this invention porous body very as high as 25, and the structure homogeneity which was conventionally superior to 17 of the example 1 of a comparison of an ingredient was shown.
[0043] (Example 2) It ****(ed) so that it might become 52 % of the weight of silicas, 34 % of the weight of alpha-aluminas, and 14 % of the weight of magnesias, and after mixing, using the resistance heating-type electric furnace, it held at 1600 degrees C for 5 hours, and it dropped underwater and the amorphous vitreous humour was obtained after melting. Particle size carried out coarse grinding of the obtained glass to the particle 150 micrometers or less by the dry type planetary mill. Wet grinding of the end of coarse powder it was obtained was further carried out by the mono-chestnut pot. Alcohol was used as an alumina and quality of a dispersion medium as a ball. Raw material concentration is 35 volume %, and grinding time amount is 20 hours.
[0044] The mean particle diameter of the particle diameter after grinding was 4.8 micrometers in 20 micrometers or less. The slurry after grinding was dried by the evaporator. The obtained desiccation fine particles were kneaded with wet with the acrylic sphere and

the binder, and extrusion molding was carried out as a tabular thing which has two or more ellipse-like holes in a longitudinal direction and which can be preferably used as a foundation of a rectangular mold filter. The added mean particle diameter of an acrylic sphere is 60 micrometers, and a mixing ratio is 30 % of the weight.

[0045] In addition, the organization of the configuration of the pore of the obtained plate etc. was the same as that of an example 1 almost. After drying this ingredient, it calcinated on 1375 degrees C and the conditions of 3 hours, and the thermal shock resistance of the plate after baking was evaluated. After exposing the assessment approach into the heated electric furnace for 30 minutes, it was taken out, it is dropped underwater, and made temperature from which generating of a crack was checked visually thermal shock destructive temperature. The result is shown in a table 2.

[0046] It compared with the system (example 2 of a comparison) containing binding material, such as the conventional kaolin and talc. As shown in a table 2, thermal shock destructive temperature is improving by 130 degrees C compared with an ingredient conventionally, and it is thought that this is based on the low coefficient of thermal expansion by cordierite single phase composition.

[0047] (Example 3) It ****(ed) so that it might become 48 % of the weight of silicas, 40 % of the weight of alpha-aluminas, and 12 % of the weight of magnesias, and after mixing, using the resistance heating-type electric furnace, it held at 1600 degrees C for 5 hours, and it dropped underwater and the amorphous vitreous humour was obtained after melting. Coarse grinding of the obtained glass was carried out with the jaw-crasher crusher, and particle size ground to the particle 150 micrometers or less by the dry type planetary mill further. The mean particle diameter of the obtained fine particles was 35 micrometers. Wet grinding of these fine particles was carried out further underwater, and after adding the binder, spray dry desiccation was carried out.

[0048] The mean particle diameter of the granulation which the obtained fine particles are 8 micrometers for mean particle diameter, and corned with the particle size of 20 micrometers or less was 40 micrometers. The ball (mean particle diameter of 60 micrometers) of polystyrene was added to these fine particles 45% of the weight with the mixing ratio, it mixed by the dry type V mixer, and the rubber die with the metal heart was filled up. They are 500 kgf/cm2 by the hydrostatic-pressure press. It fabricated by the pressure in the cylinder with the diameter of 180mm, a thickness [of 20mm], and a die length of 300mm, and Green grinding of the periphery of a Plastic solid was carried out with the cylindrical grinding machine after mold release. The obtained cylinder was calcinated on 1300-degree-C conditions of 3 hours in atmospheric air. The apparent porosity of the obtained cylinder was 38%, and the organization of the configuration of pore etc. was the same as that of the thing of an example 1 almost. The thermal stress breakdown test of this cylinder was carried out.

[0049] It let through pass for hot combustion gas inside cylindrical, let the water cooled jacket pass for the outside surface, and radiation cooling was carried out. The thermocouple was embedded in the cylinder and the inside-and-outside temperature gradient was measured. Release inspection was extinguished the fire and carried out, after setting combustion gas as predetermined temperature and holding it for 30 minutes. When there was no breakage in a cylinder, it included in the tester again and examined at still higher temperature. The inside-and-outside temperature gradient which results in destruction was 350 degrees C or more. There was nothing that bears a temperature gradient 250 degrees C or more with the conventional ingredient shown in the example 1 of a comparison.

[0050] (Examples 4-7 and examples 3-5 of a comparison) It ****(ed) so that it might become the presentation which shows a silica, alpha-alumina, and a magnesia in a table 3, and after mixing, using the resistance heating-type electric furnace, it held at 1600 degrees C for 5 hours, and it dropped underwater and the amorphous glass of various presentations was obtained after melting. Coarse grinding of the obtained glass was carried out so that particle size might be set to 150 micrometers or less by the dry type planetary mill, and wet grinding was further carried out using alcohol. The used crushing steel ball is an alumina and grinding time amount is 18 hours. The slurry after grinding was dried in the evaporator and the raw material was obtained. Powder and an acrylic ball (mean particle diameter of 60 micrometers) with a particle size [such] of 16 micrometers or less were mixed. The mixing ratio of an acrylic ball is 30 % of the weight.

[0051] Subsequently, 60x60mm metal mold is filled up with these powder, and they are 200 kgf/cm2 with a press-forming machine. It fabricated by the pressure. And the Plastic solid was calcinated on 1350 degrees C and the conditions of 2 hours in the heating furnace. The apparent porosity of the porous body after sintering was 34% - 36%. While the configuration of the pore in a porous body makes spherical pore a subject like an example 1 and the magnitude was 40-70 micrometers comparable as the acrylic ball added about, the average pore diameter was 43 micrometers. Porosity and a pore diameter were not depended on a glass presentation, but it was almost fixed.

[0052] In this way, the thermal expansion test piece (the diameter of 5mm, die length of 20mm) and the strength test piece (5x10x50mm) were started from the obtained porous body, and the mechanical characteristic was measured. The result is shown in a table 3. In presentation within the limits of this invention, the coefficient of thermal expansion (0-1000 degrees C) was as low as less than [2.5x10-6/degree C], and only the cordierite single phase was checked in analysis by the X diffraction as I understood from a table 3.

[0053] Even if such a porous body was suitable as a porous body for filters like examples 1-3 and it compared it with examples 1-3, it was equipped with the engine performance required as a filter material which is equal in any way.

[0054] The thing outside this invention presentation range which manufactured similarly is also shown in a table 3 as examples 3-5 of a comparison. These all had the high coefficient of thermal expansion, and had some by which the crack entered into the sintering porous body. Crystal phases other than a desired cordierite presentation deposit, and this is considered that internal breakage took place by the volume change at the time of sintering, or the difference in a coefficient of thermal expansion.

[0055]

[A table 1]

試料	気孔率	室温強度	熱間強度	ワイブル係数	腐食ガス暴露後強度
実施例5	32%	19MPa	22MPa	25	21MPa
比較例4	33%	12MPa	9MPa	17	7MPa

[0056]

[A table 2]

試料	熱衝撃破壊温度
実施例6	450 ℃
比較例5	320 ℃

[0057]
[A table 3]

試料		シリカ	α－アルミナ	マグネシア	熱膨張係数 $\times 10^{-6}$／℃	室温強度 MPa
実施例	1	49.5	37.2	13.3	1.0	22
	2	55	30	15	1.2	15
	3	43	41	16	1.5	18
	4	62	28	10	2.5	26
比較例	1	35	50	15	4.8	13
	2	50	30	20	5.3	28
	3	72	20	8	8.4	30

[0058]
[Effect of the Invention] Since it consists of a cordierite single phase, the ceramic filter of this invention has a very low coefficient of thermal expansion, and it is chemically stable. Moreover, since homogeneity and predetermined magnitude have spherical pore, reinforcement is also high, and it excels in dependability durable over a long period of time. Therefore, the optimal filter for carrying out the dust removal of the particle contained in elevated-temperature gas can be offered.

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(54) CERAMIC FILTER AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To improve thermal shock resistance by compacting and sintering a mixture of amorphous glass power consisting of specified amts. of silica, alumina and magnesia components with a spherical pore imparting material and using the resultant porous body having a signal phase of cordierite and mainly contg. spherical pores.
SOLUTION: Amorphous glass powder consisting of 40–65 wt.% silica component, 25–45 wt.% alumina component and 10–16 wt.% magnesia component is adjusted to ≤20 μm particle diameter, mixed with a spherical pore imparting material, compacted and sintered and the resultant porous body having a single phase of cordierite and mainly contg. spherical pores is used to produce the objective ceramic filter used as a catalyst carrier for exhaust gas from an automobile and as a filter for removing ash contained in waste combustion gas, etc. The apparent porosity and average pore diameter of the porous body are regulated to 25–50% and 10–100 μm, respectively. The amorphous glass powder adjusted to ≤20 μm diameter is preferably granulated before the mixing.

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(54)【発明の名称】　セラミックスフィルタ及びその製造方法

(57)【要約】
【課題】高温含塵ガスのフィルタとして長期耐用信頼性の高いコーディエライトセラミックスフィルタを提供する。
【解決手段】シリカ成分４０～６５重量%、アルミナ成分２５～４５重量%、マグネシア成分１０～１６重量%からなる非晶質ガラス粉末のみを使用し、該粉末を平均粒径２０μm以下に調整し、有機質の球状気孔付与材とともに、混合、成形、焼結する。

【特許請求の範囲】
【請求項１】多孔体形成材料として、シリカ成分が４０～６５重量％、アルミナ成分が２５～４５重量％、マグネシア成分が１０～１６重量％である非晶質ガラス粉末のみを成形、焼結してなるコーディエライト単一相かつ球状気孔を主体とする多孔体からなることを特徴とするセラミックスフィルタ。
【請求項２】多孔体の見掛気孔率が２５～５０％である請求項１記載のセラミックスフィルタ。
【請求項３】多孔体の平均気孔径が１０～１００μｍである請求項２記載のセラミックスフィルタ。
【請求項４】多孔体形成材料として、シリカ成分が４０～６５重量％、アルミナ成分が２５～４５重量％、マグネシア成分が１０～１６重量％である非晶質ガラス粉末のみを使用し、かつ該粉末を粒径２０μｍ以下に調整し、これに球状の気孔付与材を添加し、混合、成形、焼結することを特徴とするコーディエライト単一相からなるセラミックスフィルタの製造方法。
【請求項５】粒径２０μｍ以下に調整した非晶質ガラス粉末を造粒し、これに球状の気孔付与材を添加する請求項４記載のセラミックスフィルタの製造方法。
【請求項６】球状の気孔付与材として有機物球状体を使用し、球状気孔を主体とする多孔体からなる請求項４又は５記載のセラミックスフィルタの製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は耐熱性、耐熱衝撃性に優れかつ所定の均一な気孔径分布を有するコーディエライト単一相からなるセラミックスフィルタ及びその製造方法に関する。コーディエライトセラミックスは、熱膨張係数が１～２×10^{-6}／℃と小さいこと及びヤング率が１５０ＧＰａ以下とアルミナの半分以下であることから、耐熱衝撃性・耐熱応力性が高く、また高温時の化学的安定性にも優れる利点を生かし、多孔性を付与した材料では、自動車排ガス用触媒担体や燃焼ガス等に含まれる燃焼灰除去用のフィルタとして幅広く使用されている。
【０００２】
【従来の技術】従来のコーディエライト焼結体の製造方法の一例として、シリカ、アルミナ、マグネシアの粉末又はこれらの塩化物を用い１３００～１４００℃の高温に加熱して、その固相反応からコーディエライト焼結体とすることが知られている。
【０００３】そして、多孔体の場合、目的の気孔径とするためにこの焼結体を粉砕して一定の粒径に篩い分けし、Ｎａ、Ｃａ、Ｋ等を含む長石、リチウムアルミニウムシリケートであるβ－スポジュメン、ユークリプタイトなどコーディエライトより融点が低いか、融点以下で液相を生成する材料を結合材とし、混合、成形、焼結し、粒子間に気孔が存在する多孔体を作製する製造方法が一般的である。
【０００４】しかしこの従来の製造方法ではコーディエライトが難焼結性であることから結合材としてリチウムアルミニウムシリケートであるβ－スポジュメン、ユークリプタイト、又は、Ｎａ、Ｃａ、Ｋを含む長石（アルミノケイ酸塩）などコーディエライトより融点が低いか、融点以下で液相を生成する材料を使用するため、耐熱性が低下する欠点があった。
【０００５】例えば、特開平１－２９７１３１では、コーディエライトにリチウムアルミニウムシリケートであるβ－スポジュメン、ユークリプタイトを添加し目的の気孔径を持つコーディエライト多孔体の製造方法を開示している。このユークリプタイトは融点が約１４００℃である。したがって主成分となるコーディエライトの融点（１４７０℃）よりも低いため耐熱性が低下する。さらにコーディエライトと混合し焼結を行うと、１１００℃付近から液相を生成し焼結するため、それ以上の温度では使用できない欠点がある。
【０００６】また、Ｎａ、Ｃａ、Ｋを含む長石（アルミノケイ酸塩）を結合材とすると、結合材の熱膨張係数が４～６×10^{-6}／℃とコーディエライトと比較し高いため、焼結体としての熱膨張係数を向上させ、耐熱衝撃性を低下させることがある。
【０００７】特開平３－１０３６５では、滑石、マグネサイト、炭酸マグネシウム、石英、方解石、水酸化アルミニウムなどを混合し、水酸化マグネシウムや炭酸マグネシウムなどのマグネシウム塩の分解や昇華などの化学反応から多孔化したコーディエライト多孔体の製造方法を開示しているが、この方法により製造される多孔体は、気孔が熱分解反応等で作製されているため、広い気孔径分布をとる多孔体となり、所望の気孔径の気孔径分布をもつ均一な多孔体を得がたい欠点がある。
【０００８】特開昭６０－２２６４１６では、アルキルシリケートのアルコール溶液中にアルミニウム金属塩とマグネシウム金属塩を溶かし込み、加熱帯中に噴霧、溶融し、微粉のガラス中空球を作製し、成形、焼結することによる、平均気孔径が１μｍ未満～数μｍの微細な気孔を有するコーディエライト多孔体の製造方法を開示している。この方法は、気孔率４８％以上で気孔径が数μｍ以下と高気孔率かつ微細な気孔を有する多孔体を作製するのには適するが、気孔率４８％未満の多孔体の作製や、平均気孔径が１０μｍ以上、特に５０μｍ以上の気孔径の大きなコーディエライト多孔体の作製は困難である欠点がある。
【０００９】特開昭５７－９２５７４では、コーディエライト組成のガラス粉末と焼成によりコーディエライトを析出するカオリン、タルク、酸化アルミニウムからなる原料を使用することを開示している。この方法は、原料が比較的安価で、押し出し成形など、ある種の製造方法には適するが、原料が天然鉱物であるために不純物の

混入が避けられず、その結果高温での強度低下が起こる点で充分ではない。

【００１０】このように、以上の既存技術の本質的な問題は、熱膨張係数に優れたコーディエライトを用いながら、その焼結性を向上するために他の成分を添加し多孔体を得ているため材質の特性を充分生かしきれていないことと、多孔体を形成する気孔の形状制御が任意に行えないこと、さらに、特開昭６０－２２６４１６などでは気孔率範囲が適切でなく、また高温ガスフィルタとして機能するための機械的強度が充分でないなどの問題があり、どれも高温ガスフィルタとして使用する上では、長期耐用信頼性に問題があった。

【００１１】

【発明が解決しようとする課題】本発明はこれら従来技術を背景とし、耐熱性が高く、耐熱衝撃性に優れ、化学的にも安定で、気孔形状がほぼ球状体で、その気孔径分布が均一なコーディエライト多孔体を用いたセラミックスフィルタを提供することを目的とする。

【００１２】

【課題を解決するための手段】本発明は、多孔体形成材料として、シリカ成分が４０～６５重量％、アルミナ成分が２５～４５重量％、マグネシア成分が１０～１６重量％からなる非晶質ガラス粉末のみを成形、焼結してなるコーディエライト単一相かつ球状気孔を主体とする多孔体からなることを特徴とするセラミックスフィルタを提供する。

【００１３】また、多孔体形成材料として、シリカ成分が４０～６５重量％、アルミナ成分が２５～４５重量％、マグネシア成分が１０～１６重量％からなる非晶質ガラス粉末のみを使用し、かつ該粉末を粒径２０μｍ以下に調整し、これに球状の気孔付与材を添加し、混合、成形、焼結することを特徴とするコーディエライト単一相からなるセラミックスフィルタの製造方法を提供する。

【００１４】本発明のセラミックスフィルタの好ましい態様では、多孔体の見掛気孔率が２５～５０％である。本発明のセラミックスフィルタのさらに好ましい態様では、多孔体の平均気孔径が１０～１００μｍである。

【００１５】本発明の製造方法の好ましい態様では、粒径２０μｍ以下に調整した非晶質ガラス粉末を造粒し、これに球状の気孔付与材を添加する。本発明の製造方法の別の好ましい態様では、球状の気孔付与材として有機物球状体を使用し、球状気孔を主体とする多孔体からなる。

【００１６】コーディエライトは前述のとおり難焼結性であることから結晶化物単体ではほとんど焼結せず、粒子間が強固に結合された多孔体を得られない。本発明者らは、多孔体を形成する駆体材料として使用する粉末が非晶質ガラスのみとし、これを微粉砕し、焼結することにより、結合材を添加することなく強固な結合を発現させ、かつ望ましい方法として添加した有機物球体が焼成時に焼失したあとに形成される球状気孔を利用することにより平均気孔径が１０～１００μｍ、特には４０～６０μｍの球状気孔が均一に分散したコーディエライト単一相の多孔体からなるセラミックスフィルタを製造できることを見いだした。

【００１７】

【発明の実施の形態】本発明に使用する非晶質ガラスの出発原料はシリカ（SiO_2）源としては、天然に産出するケイ砂、アルミナ（Al_2O_3）源としてはコランダム、マグネシア（ＭｇＯ）源としては炭酸マグネシウム、硝酸マグネシウムなどのマグネシウム塩又は水酸化マグネシウムなどでよい。どの原料も原料純度が９５％以上、特には９８％以上、のものが好ましい。純度が９５％未満では、原料中に含まれる不純物により、結晶化後得られるコーディエライト単一相からなる多孔体の組成がずれ、耐熱性の低下、熱膨張係数の増大が起こるおそれがある。

【００１８】原料ガラスの組成をシリカ成分が４０～６５重量％、アルミナ成分が２５～４５重量％、マグネシア成分が１０～１６重量％と限定した理由は、この範囲外の組成では、加熱（焼結）処理後、コーディエライト単一相の多孔体が得られず、ムライト、ホルステライト、スピネル又は出発原料であるアルミナ、シリカ、マグネシアが混合相として析出するためである。

【００１９】なお、ガラスの組成として、これらの目的を損なわない程度において少量のその他の成分や不純物が含まれていても支障ない。また、微粉砕のために行われる湿式粉砕では、アルミナボールを使用する場合、その粉砕時のボール磨耗から混入するアルミナ量については、初期添加のアルミナ量を若干低減することにより組成のずれが起こらないようにすることが好ましい。

【００２０】なお、本発明においてコーディエライト単一相とは、コーディエライト結晶として、$xMgO \cdot yAl_2O_3 \cdot zSiO_2$ において x：１．５～２．６、y：１．５～２．４、z：４．１～６．４で示される範囲に含まれる結晶相をいう。

【００２１】本発明に使用する非晶質ガラス及びその粉末の製造方法は以下のとおりである。使用する原料は充分に乾燥後、市販の電気炉により１５００℃以上で溶融する。ガラス体として緻密なものを得るため１６００℃以上で溶融するのが好ましい。電気炉は特に限定されず１５００℃以上となるものであればよい。電気炉で得られた溶融物は、電気炉より取り出し、非晶質ガラスを得るために水中に投入して急冷することが好ましい。鉄板や銅板等の上に流し出して急冷してもよい。

【００２２】こうして得られた非晶質ガラスを粒径１～３ｍｍほどの大きさに粉砕する。その後振動ミルなどの装置を用い粒径１５０μｍ以下まで粉砕する。得られた粉末をモノマロンポットにてさらに湿式粉砕する。粉砕

時の分散媒質は水又はアルコールが望ましい。水を使用する場合には、適切な分散剤を適正量添加することにより、３０～４０体積％の高濃度スラリが得られる。

【００２３】スラリ濃度、粉砕時間などは、粉砕後に得られる粉末の粒径が２０μｍ以下になるように設定することが好ましい。粒径が２０μｍ超では、ガラス原料の半分以上が後述する気孔付与剤の有機物球状体の大きさに近く、均一な球状体気孔を形成できず、また、それらの大きな粒子が凝集した場合には多孔体の強度を低下させる応力集中源となりうる。

【００２４】以上の粉砕スラリを乾燥する。アルコール粉砕した場合には、エバポレータによる真空乾燥を行う。また、水粉砕の場合には、スプレイドライによる造粒乾燥でもよい。

【００２５】こうして調製したコーディエライト組成をもたらす非晶質ガラス粉末に球状気孔を付与せしめるために好ましくは有機物球状体を添加する。添加する有機物球状体は、種々のものが使用できるが、アクリル、ポリスチレン、ＰＭＭＡ（ポリメタクリル酸メチル）など、比較的低温で燃焼、分解する樹脂質のものが望ましい。

【００２６】球状体としたのは、燃焼後に得られる気孔の形状を球状とすることにより、多孔体の破壊時の亀裂先端の応力集中を低減させ、非晶質ガラス粉末のみからなる焼結体の強度を向上させるためである。気孔付与材として通常用いられる黒鉛粉などの、有機物以外の付与材の多くは、焼結時に燃焼分解する温度が比較的高く、また、焼成炉中の酸素分圧の変動によって非常に分解しにくいこともあり、一般的には好ましくない。

【００２７】また、球状体の大きさは、目的とするセラミックスフィルタの気孔径を考慮して選択できるが、本発明のセラミックスフィルタが石炭燃焼から発生する含塵ガス中の微粒子の除去に適したものであることからすれば、その微粒子の大きさと、フィルタ使用時の圧損特性などを考慮し、平均気孔径として１０～１００μｍ程度の気孔を形成するのに適した２０～１００μｍ程度のものが適切である。

【００２８】また、非晶質ガラス粉末に対しての混合割合としては、得られる多孔体の気孔率に関係するが、ガラス粉末５０～８０重量％に対し、気孔付与材２０～５０重量％程度が好ましい。

【００２９】本発明の製造方法では、このように非晶質ガラス粉末として２０μｍ以下のものを用いるが、成形に際しては加圧において元の微粒に容易に崩壊しうる状態にあらかじめ造粒した顆粒として用いることも有効であり、このような２０μｍ以下の微粉末を用いて４０～１００μｍ程度の顆粒にした造粒粉末も本発明の２０μｍ以下の粉末に含まれる。

【００３０】すなわち、造粒物はその形状を焼結時にも保持できれば、気孔付与材の添加量を減らせる利点があり、また添加する球状気孔付与材と同程度の大きさの顆粒とすれば両者を混合しやすい利点もある。また、本発明において、微粒の非晶質ガラス粉末をあらかじめ気孔付与材の周囲に付着せしめた状態で他のガラス粉末と混合することもできる。

【００３１】本発明における成形、焼結方法は特に限定されず、上記方法により得られた混合粉末を金型成形、押し出し成形などの方法により成形すればよい。得られた成形体は、抵抗加熱などの電気炉を用い、１０００～１４５０℃の範囲で焼結を行えばよい。なお、ガラスの結晶化を促進するため最高温度において保持時間を設ける方が好ましい。

【００３２】以上の方法により、添加した有機物球状体とほぼ同一か、やや小さい平均気孔径の球状を主体とした空孔が均一に分散したコーディエライト単一相からなる焼結体が製造できる。このように本発明によると、耐熱性、耐熱衝撃性を損なうことなく気孔径が均一に分布した目的の気孔径のコーディエライト多孔体が製造できる。焼結体中の孔が球状体であることは、構造体として応力を負荷された場合に、欠陥としての応力集中が少なく、結果として高い強度を与える。

【００３３】なお、本発明において、球状気孔を主体とする多孔体とは、個々の気孔の多くの形状が鋭い角を持つ気孔はほとんど存在しないような球状となっていて、これらの気孔が互いに開孔気孔となるように気孔で連結しているとともに一部は球状気孔同士が互いに連結した状態の気孔を形成しているような多孔体をいう。

【００３４】このような本発明の多孔体は、前述した目的のセラミックスフィルタとして好適に使用されうる見掛気孔率が２５～５０％と大きくかつ平均気孔径も１０～１００μｍ、特に４０μｍ以上の気孔径としては大きな孔径のものを容易に制御されたものとして得られる。また、気孔径分布も上記平均気孔径の範囲にあり、望ましくは平均気孔径から±２０％の範囲内に全気孔容積の８０％以上が入るものが容易に得られる。

【００３５】このように、本発明の製造方法により製造したフィルタは、コーディエライト単一相からなるために、熱膨張係数がきわめて低く、化学的にも安定であり、高温ガス中の脱塵を行うフィルタの材料としては最適である。また、気孔が球状であるために強度も高く、長期耐用信頼性にも優れる。

【００３６】

【実施例】以下に実施例及び比較例を挙げてさらに詳しく説明するが、本発明はこれらに限定されない。

【００３７】（実施例１）シリカ４９．５重量％、α－アルミナ３７．２重量％、マグネシア１３．３重量％となるよう秤取し、混合後、抵抗加熱式の電気炉を用い、１６００℃で５時間保持し溶融後、水中に投下し非晶質ガラス体を得た。得られたガラスを乾式遊星ミルにより粒径１５０μｍ以下の粒子に粗粉砕した。得られた粗粉

末をさらにモノマロンポットにて湿式粉砕した。ボールとしてアルミナ、分散媒質として水を使用した。原料濃度は３５体積％、粉砕時間は２４時間である。

【００３８】粉砕後の粒子径は２０μｍ以下で、平均粒子径は４．８μｍであった。粉砕後のスラリは、ポットから取り出し後、そのままスプレイドライヤにて乾燥造粒した。アトマイザの回転数は８０００ｒｐｍ、入口空気温度は１４０℃、出口空気温度は８０℃である。乾燥した顆粒の平均粒径は４７μｍであった。

【００３９】得られた顆粒をアクリル製の球体（平均粒径６０μｍ）とＶミキサーにて乾式混合した。アクリル球体の混合比は３０重量％で、混合時間は３０分とした。得られた粉末を６０ｍｍ×１２０ｍｍの金型に充填し、プレス成形機にて２００ｋｇｆ／ｃｍ² の圧力にて成形した。得られた成形体を抵抗加熱炉中で１３５０℃２時間で焼成した。得られた焼結体はコーディエライト単一相であり、また、その見掛気孔率は３２％であった。

【００４０】焼結体中の気孔の分布はほぼ均一であり、平均気孔径は４３μｍであった。気孔径分布は、平均気孔径から±１０％の範囲内に全気孔容積の８３％が存在し、高い気孔径制御性を示した。また、得られた気孔の形状は球状を基本とし、いくつかの球状気孔が連結した孔も部分的に形成されるが、応力集中源となる鋭い気孔はほとんどなく、多孔体の強度の点からも望ましい組織が得られた。

【００４１】得られた多孔体の高温強度及び化学的安定性を評価するために、熱間（１０００℃）での曲げ強度を比較した。また石炭燃焼プラントの排ガスと同一組成の硫化物を含む９００℃高温ガスに暴露したのちその強度を測定した。以上の結果を表１に示す。

【００４２】また表１には従来から用いられている結合材にリチウムアルミノシリケートを使用した同一気孔率の材料（比較例１）の試験結果も併記した。コーディエライト単一相からなる本発明多孔体は熱間でも強度低下がほとんどなく、また腐食性のガス下においても全く強度低下を起こさなかった。したがって、石炭発電プラントの熱間脱塵に使用されるフィルタとして利用すれば、長期間信頼性を損なうことなく使用できる。さらに、セラミックスの強度のばらつきを示すワイブル係数（熱間曲げ強度での測定）は本発明多孔体が２５ときわめて高く、従来材料の比較例１の１７よりも優れた構造均一性を示した。

【００４３】（実施例２）シリカ５２重量％、α－アルミナ３４重量％、マグネシア１４重量％となるよう秤取し、混合後、抵抗加熱式の電気炉を用い、１６００℃で５時間保持し溶融後、水中に投下し非晶質ガラス体を得た。得られたガラスを乾式遊星ミルにより粒径が１５０μｍ以下の粒子に粗粉砕した。得られた粗粉末をさらにモノマロンポットにて湿式粉砕した。ボールとしてアルミナ、分散媒質としてアルコールを使用した。原料濃度は３５体積％、粉砕時間は２０時間である。

【００４４】粉砕後の粒子径は２０μｍ以下で平均粒子径は４．８μｍであった。粉砕後のスラリは、エバポレータにより乾燥した。得られた乾燥粉体をアクリル球体、バインダとともに湿式にて混練し、長手方向に楕円状の孔を複数有する、直交型フィルタの基礎として好ましく使用しうる板状のものとして、押し出し成形した。添加したアクリル球体の平均粒径は６０μｍ、混合比は３０重量％である。

【００４５】なお、得られた板の気孔の形状等の組織は、実施例１とほぼ同様であった。同材料を乾燥後に１３７５℃、３時間の条件にて焼成し、焼成後の板の耐熱衝撃性を評価した。評価方法は、加熱した電気炉中に３０分暴露してから取り出して水中に投下するもので、目視にてクラックの発生が確認された温度を熱衝撃破壊温度とした。その結果を表２に示す。

【００４６】従来のカオリンやタルクなどの結合材を含む系（比較例２）と比較した。表２よりわかるように、熱衝撃破壊温度は従来材料に比べて１３０℃向上しており、これはコーディエライト単一相組成による低い熱膨張係数によるものと考えられる。

【００４７】（実施例３）シリカ４８重量％、α－アルミナ４０重量％、マグネシア１２重量％となるよう秤取し、混合後、抵抗加熱式の電気炉を用い、１６００℃で５時間保持し溶融後、水中に投下し非晶質ガラス体を得た。得られたガラスをジョークラッシャ粉砕器にて粗粉砕し、さらに乾式遊星ミルにより粒径が１５０μｍ以下の粒子に粉砕した。得られた粉体の平均粒径は３５μｍであった。同粉体をさらに水中にて湿式粉砕し、バインダを加えてからスプレイドライ乾燥した。

【００４８】得られた粉体は粒径２０μｍ以下で平均粒径は８μｍであり、造粒した顆粒の平均粒径は４０μｍであった。同粉体にポリスチレンの球（平均粒径６０μｍ）を混合比で４５重量％加え、乾式Ｖミキサーにて混合し、金属芯のあるゴム型に充填した。静水圧プレスにて５００ｋｇｆ／ｃｍ² の圧力にて直径１８０ｍｍ、肉厚２０ｍｍ、長さ３００ｍｍの円筒に成形し、離型後に成形体の外周を円筒研削機にてグリーン研削した。得られた円筒を大気中１３００℃３時間の条件にて焼成した。得られた円筒の見掛気孔率は３８％であり、気孔の形状等の組織は実施例１のものとほぼ同様であった。同円筒の熱応力破壊試験を実施した。

【００４９】円筒の内部に高温の燃焼ガスを通し、外面を水冷ジャケットを通して輻射冷却した。円筒には熱電対を埋め込み、内外温度差を測定した。燃焼ガスを所定温度に設定し、３０分保持してから、消火、解放点検した。円筒に破損がなければ、再度試験器に組み込み、さらに高い温度にて試験を実施した。破壊に到る内外温度差は３５０℃以上であった。比較例１に示した従来の材

料では２５０℃以上の温度差に耐えるものはなかった。

【００５０】（実施例４～７及び比較例３～５）シリカ、α－アルミナ、マグネシアを表３に示す組成となるように秤取し、混合後、抵抗加熱式の電気炉を用い、１６００℃で５時間保持し溶融後、水中に投下し各種組成の非晶質ガラスを得た。得られたガラスを乾式遊星ミルにより粒径が１５０μm以下になるように粗粉砕し、さらにアルコールを用いて湿式粉砕した。使用した粉砕ボールはアルミナで、粉砕時間は、１８時間である。粉砕後のスラリをエバポレータにて乾燥し、原料を得た。これらの粒径１６μm以下の粉末とアクリル球（平均粒径６０μm）とを混合した。アクリル球の混合比は３０重量%である。

【００５１】ついで、これらの粉末を６.０×６０mmの金型に充填し、プレス成形器にて２００ｋｇｆ／ｃｍ^{2}の圧力にて成形した。そして成形体を加熱炉内で１３５０℃、２時間の条件にて焼成した。焼結後の多孔体の見掛気孔率は３４%～３６%であった。多孔体中の気孔の形状は実施例１と同様に球状気孔を主体とするもので、その大きさはおよそ添加したアクリル球と同程度の４０～７０μmであるとともに、その平均気孔径は４３μmであった。気孔率、気孔径ともガラス組成によらず、ほぼ一定であった。

【００５２】こうして得られた多孔体から熱膨張試験片（直径５mm、長さ２０mm）と強度試験片（５×１０×５０mm）を切り出し、機械特性を測定した。その結果を表３に示す。表３から分かるとおり、本発明の組成範囲内では熱膨張係数（０～１０００℃）が２．５×１０$^{-6}$／℃以下と低く、X線回折による分析ではコーディエライト単一相のみが確認された。

【００５３】このような多孔体は、実施例１～３と同様フィルタ用の多孔体として好適なものであり、実施例１～３と比較しても何ら遜色のないフィルタ材料として必要な性能を備えていた。

【００５４】同様にして製造した本発明組成範囲外のものも比較例３～５として表３に示す。これらは全て熱膨張係数が高く、また、焼結多孔体中にクラックが入ったものもあった。これは所望のコーディエライト組成以外の結晶相が析出し、焼結時の体積変化や熱膨張係数の違いにより、内部破損が起こったものと考えられる。

【００５５】

【表１】

試料	気孔率	室温強度	熱間強度	ワイブル係数	腐食ガス暴露後強度
実施例５	32%	19MPa	22MPa	25	21MPa
比較例４	33%	12MPa	9MPa	17	7MPa

【００５６】

【表２】

試料	熱衝撃破壊温度
実施例６	450 ℃
比較例５	320 ℃

【００５７】

【表３】

試料		シリカ	α－アルミナ	マグネシア	熱膨張係数 ×10⁻⁶／℃	室温強度 MPa
実施例	1	49.5	37.2	13.3	1.0	22
	2	55	30	15	1.2	15
	3	43	41	16	1.5	18
	4	62	28	10	2.5	26
比較例	1	35	50	15	4.8	13
	2	50	30	20	5.3	28
	3	72	20	8	8.4	30

【００５８】

【発明の効果】本発明のセラミックスフィルタは、コーディエライト単一相からなるために、熱膨張係数がきわめて低く、化学的にも安定である。また気孔が均一かつ所定の大きさの球状であるために強度も高く、長期耐用の信頼性に優れる。したがって高温ガス中に含まれる微粒子を脱塵するに最適なフィルタを提供しうる。